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SULFURIC ACID

Other Names	Sulphuric acid, hydrogen sulfate, battery acid, electrolyte acid, fertilizer acid, oil of vitriol, spirit of sulfur, oleum, CAS 7664-93-9
Description	Colourless (when pure) to dark brown, oily liquid; odourless, unless heated, then choking. Fuming sulfuric acid (oleum) is an oily yellow liquid giving off sulfur trioxide vapours at room temperature. It has a sharp, penetrating and choking odour.

HAZARD SUMMARY

Exposure	Inhalation, skin contact and eye contact.
Effects of Short-Term Exposure	Concentrated sulfuric acid is extremely corrosive. Mist, vapour or liquid can cause severe damage to eyes, nose, throat, mouth and lungs. Inhalation can cause tickling sensations in the nose and throat, coughing and sneezing, and difficulty in breathing. Skin contact can produce burns. Contact with eyes can lead to blindness.
Effects of Long-Term Exposure	Mists and vapours can cause erosion and discolouration of the teeth, chronic irritation of the eyes, or chronic inflammation of the nose, throat and airways.
Fire and Explosion Hazards	Sulfuric acid does not burn but can react violently with many materials and may cause finely-divided combustible materials to ignite. Concentrated sulfuric acid reacts violently with water, producing heat which causes splattering. Contact with most metals can generate explosive hydrogen gas.
Fire Extinguishers	Use an extinguisher appropriate for the material that is burning. Avoid using water since it generates heat and causes splattering. Use water spray to cool and prevent rupture of containers involved in a fire.

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Chemical Reactivity	Reacts violently or explosively with many organic and inorganic chemicals including water, alcohol, carbides, chlorates, picrates, nitrates and metals.
Personal Protection	Acid-resistant clothing made with neoprene or polyvinyl chloride (PVC) with a nylon liner is recommended. Splash-proof chemical safety goggles or a face shield (8-inch minimum) should be worn for eye and face protection. Appropriate respiratory protection should be worn whenever mist or vapour concentrations may exceed permissible limits.
Storage	Sulfuric acid should be stored in tightly closed containers in a cool area with adequate ventilation. Keep containers away from normal work areas, sources of heat, sparks and reactive chemicals.
Handling	Always add acid to water, slowly and with constant stirring. Never pour water on acid since this may cause an explosive reaction and splattering of the acid.
Exposure Limits	As recommended by the American Conference of Governmental Industrial Hygienists (ACGIH) 1986-87. Threshold Limit Value - Time-Weighted Average Exposure (TLV-TWA): 1 mg/m^3 (milligrams per cubic metre) or 0.250 ppm (parts per million)

TWA is defined as the time-weighted average concentration for a normal 8-hour workday and a 40-hour workweek.

SCOPE OF THE DOCUMENT

This summary was prepared at the Canadian Centre for Occupational Health and Safety (CCOHS) and is intended primarily as a source of information for persons who work with or may be occupationally exposed to this material. The information selected for inclusion is believed to be reliable and generally relevant to occupational health. Other information may be available which bears on particular work situations. The scientific data in many areas are limited and may allow a variety of interpretations. Additional information, corrections, comments, and questions are welcome, and should be addressed to the Inquiries Service, CCOHS, 250 Main Street East, Hamilton, Ontario, L8N 1H6, (416) 572-2981, or toll free 1-800-263-8276.

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I. USES AND OCCURRENCE

Sulfuric acid has many uses and is one of the most important industrial chemicals.

It is used in the manufacture of synthetic fertilizers, explosives, plastics, artificial fibres, dyes, pharmaceuticals, detergents, adhesives, paint, paper and many other chemicals and products. It is also used as an electrolyte in lead storage batteries, in electroplating, as a pickling agent for iron and steel, as a leaching agent for ores, as an alkylating agent and dehydrating agent, in refining of petroleum, food processing, textiles and tanning of leather. It is also a very common laboratory chemical.

Fuming sulfuric acid (a mixture of sulfuric acid and sulfur trioxide) is used as a sulfating and sulfonating agent, in petroleum refining and in the manufacture of various chemicals, dyes and explosives, and as a laboratory reagent.

A small amount of sulfuric acid is available in powdered form. The powder is dissolved in water, filtered and yields a clear acid in strengths up to 80%.

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II. TOXICOLOGY

Routes of Exposure
Skin and eye contact are the most common routes of exposure to sulfuric acid in the workplace. Inhalation of mist or vapour can also occur. Ingestion is unlikely under normal work practices.

Sulfuric acid has a very low vapour pressure and, at normal room temperatures, very little vapour will be found in the workroom air. Consequently, inhalation of vapours is seldom a problem except where hot acid or fuming sulfuric acid (oleum) is used. Most exposures are a result of inhalation of sulfuric acid mist. Pickling, electroplating and anodizing of metals, and charging and plate-forming in battery manufacturing are common processes generating sulfuric acid mist. The size of the mist droplets will affect their uptake into the body. Large droplets do not penetrate very far into the respiratory tract and cause irritation of the nose and throat. Small droplets can reach the lungs and cause more serious damage[1,2].

Removal from the Body
The damage caused by sulfuric acid is almost entirely due to its corrosive rather than its toxic effects. However, small quantities of sulfuric acid entering the body are neutralized by normal body processes such as excretion of acids and non-toxic sulfates in the urine.

General information on routes of exposure is available in the CCOHS publication "How Workplace Chemicals Enter the Body"[2].

Effects of Short-Term Exposures in Humans
The effects of short-term exposure to sulfuric acid are a result of its highly irritating and corrosive action. Exposure to sulfuric acid as a mist, vapour or liquid can cause intense irritation and severe burns to the skin, eyes, and respiratory system.

Inhalation
The first sign of inhalation overexposure to sulfuric acid mist is usually an irritation or tickling sensation in the nose and throat, followed by coughing and sneezing. These symptoms are similar to the effects of breathing dusty air. The nose and throat may become severely irritated, and the air passages may fill with fluid making breathing difficult.

The following responses have been reported in humans exposed to sulfuric acid for brief periods[1,3,4,5]:

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0.5 - 2.0 mg/m^3	Barely detectable
3.0 - 4.0 mg/m^3	Easily noticeable irritation, coughing
6.0 - 10.0 mg/m^3	Decidedly unpleasant, coughing, marked changes in respiration
40.0 - 80.0 mg/m^3	Unbearable

At concentrations higher than 80.0 mg/m^3, exposure to sulfuric acid leads to severe inflammation of the tissues lining the respiratory airways and the lung tissues. Death caused by inhalation of high concentrations is probably due to severe acidic burns of the lung tissue which result in fluid accumulation. Chronic bronchitis, scarring and emphysema may develop in lungs damaged by sudden exposures to high levels of fuming sulfuric acid (oleum)[10]. In addition to these effects on the respiratory system, sulfuric acid mist can cause damage to the skin, erosion of the teeth and severe injuries to the eyes[1,3,7,8].

There is some evidence that tolerance (acclimatization) to the irritant effects of sulfuric acid mist develops. Some people have been able to tolerate 3 to 4 times the levels which are intolerable to people having no prior exposure[9]. Cardiac patients, smokers, asthmatics and the aged are more sensitive to the irritant effects of sulfuric acid mist[3,9].

Effects on the Skin

Skin burns are the most common workplace injuries caused by sulfuric acid[1,4,8]. They are usually a result of splashing, spilling or spraying. Acid burns are similar to heat burns and may be classified accordingly as first, second or third degree. The severity of the injury depends on the concentration of the acid and the duration of contact.

Contact with dilute solutions may cause mild skin irritation. Concentrated solutions can cause deep burns. Initially, the area of contact with the acid turns white, then brown. An open sore then forms on a light red background. The injuries are extremely painful. They usually take a long time to heal and frequently leave scars. Extensive burns can cause death[16].

Effects on the Eyes

Contact even with small amounts of concentrated sulfuric acid can cause severe eye damage resulting in blindness. Acid burns of the

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eyelids and surrounding parts of the face can produce scarring and disfigurement[6]. Splashes from dilute sulfuric acid cause temporary effects from which recovery may be complete[1,8].

Ingestion
Ingestion of the liquid is unlikely in ordinary industrial use. Accidental ingestion of concentrated acid produces serious burns of the mouth and intestinal tract[8].

Effects of Long-Term Exposures
The major health concerns of sulfuric acid are a result of its highly corrosive action during short-term exposures to high concentrations. There is much less hazard associated with long-term low-level exposure.

Severe inflammation of the tissues lining the respiratory airways, mouth, stomach, eyes and the skin has been associated with repeated or long-term exposures to mists or vapours of sulfuric acid[3-8].

Long-term exposures to sulfuric acid concentrations of 0.8 to 16.6 mg/m^3 have resulted in erosion and discolouration of the teeth. This has happened in workers exposed to sulfuric acid mist in the storage battery industry[12]. In severe cases, which usually develop over many years of exposure, there may be considerable tooth disfigurement. Loss of tooth dentine may make the teeth more sensitive to temperature extremes[13].

Reproductive Hazards
Studies in laboratory animals are widely used to indicate the potential of a chemical to cause reproductive effects in humans.

No reproductive effects were observed in mice or rabbits exposed to 5 or 20 mg/m^3 of sulfuric acid mist, 7 hours per day, from day 6 through day 15 of pregnancy for mice or from day 6 through day 18 for rabbits[14].

Carcinogenic or Mutagenic Hazards
Sulfuric acid has not been tested for carcinogenic or mutagenic activity[1,4].

Toxicity Data in Animals
The relative poisoning potential of a compound can be assessed from the LD_{50} or LC_{50} obtained in animal tests. The LD_{50} is the amount of a chemical (weight of chemical/weight of animal) which is needed to kill one-half (50%) of the test animals. The LC_{50} is the concentration

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in air which kills half of the animals following an exposure lasting 4 hours or other indicated time period. Test animals are usually rats, mice, or other rodents. Routes of exposure are usually oral (by mouth), dermal (absorption through the skin), or inhalation (breathing of vapour). The values for sulfuric acid are:

LD_{50} (rat, oral)	2,140 mg/kg[15]
LC_{50} (rat, inhalation)	510 mg/m^3/2 hours[15]
LC_{50} (rat, inhalation)	347 ppm/1 hour[4]
LC_{50} (mice, inhalation)	320 mg/m^3/2 hours[15]
LC_{50} (guinea pigs, inhalation)	30 mg/m^3/8 hours[4]

General information on the LD_{50} test is available in the CCOHS publication "What is an LD_{50}?"[16].

Death in animals inhaling sulfuric acid vapours is largely caused by blood or fluid accumulation in the lungs.

III. FIRE AND EXPLOSION HAZARDS

Sulfuric acid is a non-flammable and non-combustible liquid. However, fire may result from the heat generated by contact of concentrated sulfuric acid with other combustible materials. Sulfuric acid reacts with most metals to produce flammable hydrogen gas that may explode if ignited in confined spaces. Sulfur oxides can be formed when sulfuric acid is strongly heated or reacts with certain materials.

Fire Extinguishing Agents

Since sulfuric acid is not flammable, use extinguishing agents appropriate for the material which is burning. Avoid the use of water since when applied directly to sulfuric acid it can generate heat and cause splattering. However, water spray can be used to cool and prevent rupture of containers involved in a fire. If it can be done safely, move containers away from the fire. Avoid spraying water inside containers.

Chemical Reactivity

Sulfuric acid reacts violently or explosively with many organic and inorganic chemicals including water, alcohol, carbides, chlorates, picrates, nitrates, metals and other combustible materials.

Several reference texts provide more complete lists of chemicals which may undergo hazardous chemical reactions with sulfuric acid[17,18].

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IV. EXPOSURE CONTROL

In many operations where sulfuric acid is used, vapours or mists are produced. Local exhaust ventilation, process enclosure and other engineering controls may be necessary. Corrosion-resistant ventilation systems should be used.

Although substitution and engineering controls such as ventilation are the preferred methods of controlling exposure to sulfuric acid in the workplace, the use of personal protective equipment (e.g. special clothing and respirators) may increase the level of protection for workers exposed to sulfuric acid. In some situations, such as working in enclosed spaces and in some maintenance operations, the use of personal protective equipment may be essential since effective ventilation and engineering controls may not be possible.

Protective Clothing

Protective clothing (gloves, coveralls, boots, etc.) should be worn as needed to prevent exposure of the skin to liquid sulfuric acid or solutions containing more than 1% by weight sulfuric acid.

Splash-proof chemical safety goggles and a face shield (eight-inch minimum) should be worn during any operation in which sulfuric acid may splash.

Sulfuric acid is a highly corrosive acid and many materials do not provide adequate protection. Clothing made with acid-resistant materials such as nylon-backed neoprene or polyvinyl chloride (PVC) can resist penetration and degradation.

Gauntlet-type, acid-resistant gloves made of neoprene or PVC are used for most operations and should be checked for leaks prior to their use. When worn, the gauntlet part of the glove should be covered with the sleeve of the jacket to prevent the acid from entering the glove. Special arm protectors are recommended to cover the sleeve and the gauntlet, eliminating the possibility of acid getting inside the glove or sleeve of the jacket.

Boots should be at least calf height and when worn should be covered by the legs of protective trousers to prevent contamination of the inside of the boot.

For maximum protection, an air-supplied acid suit should be worn.

Contaminated clothing should be placed in closed containers for storage until it can be laundered or discarded. Laundry personnel

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should be informed of the hazards of sulfuric acid. Laundered clothing should be inspected to ensure that it is free of pinholes and tears.

An emergency drench shower (safety shower) and an eye-wash fountain should be provided within the immediate working area for emergency use.

Respiratory Protection
Factors to be considered in a respiratory protection program include:

Selection of appropriate respirators
Respirator fit testing
Respirator maintenance
Cartridge life
Worker training
Program evaluation
Inspection
Cleaning

These factors are described in more detail in CSA Standard Z94.4-M1982, "Selection, Care, and Use of Respirators", available from the Canadian Standards Association.

The degree of respiratory protection required depends on the concentration of the mist or vapour and the duration of the exposure. NIOSH[19] recommends the following respiratory protection*:

Particulate concentration of 25 mg/m^3 or less (6 ppm):
** Any powered air-purifying respirator with a high-efficiency particulate filter and acid gas cartridge(s), or
** Any supplied-air respirator operated in a continuous-flow mode.

Particulate concentration of 50 mg/m^3 or less (13 ppm):
Any chemical cartridge respirator with a full facepiece and acid gas cartridge(s) in combination with a high-efficiency particulate filter, or
Any self-contained breathing apparatus with a full facepiece, or
Any supplied-air respirator with a full facepiece, or
An air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted acid gas canister having a high-efficiency particulate filter.

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Particulate concentration of 80 mg/m^3 or less (20 ppm):
Any supplied-air respirator with a full facepiece and operated in a pressure-demand or other positive-pressure mode.

Emergency or planned entry in unknown concentration or IDLH conditions***:
Any self-contained breathing apparatus with a full facepiece and operated in a pressure-demand or other positive-pressure mode, or
Any supplied-air respirator with a full facepiece and operated in pressure-demand or other positive pressure mode in combination with an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive-pressure mode.

Escape:
Any air-purifying full facepiece respirator (gas mask) with a chin-style or front- or back-mounted acid gas canister having a high-efficiency particulate filter, or
Any appropriate escape-type self-contained breathing apparatus.

*Note: The above recommendations apply only to equipment approved by NIOSH or MSHA organizations.

**Note: Substance causes eye irritation or damage; eye protection needed.

***Note: For the purpose of respirator selection, the Immediately Dangerous to Life or Health (iDLH) level represents the maximum concentration from which one could escape within 30 minutes without any escape-impairing symptoms or any irreversible health effects.

Air-supplied respirators must be worn in oxygen-deficient areas.

Respirators and gas masks fitted with acid gas cartridges with a high-efficiency particulate filter can provide protection against vapours or mists of sulfuric acid for a limited period of time. The useful life of a respirator depends on the amount of absorbing material in the cartridge, the concentration of mists or vapours, the temperature, and the rate of breathing.

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V. SMALL-SCALE STORAGE AND HANDLING

Sulfuric acid should be stored in a separate, well-ventilated, cool, dry area with acid-resistant floors. Glass containers can be used for all concentrations of sulfuric acid. Containers should be kept tightly closed and clearly labelled to indicate their contents. Storage area should be sheltered from direct sunlight and away from sources of ignition and from chemicals with which sulfuric acid can react explosively. Structural materials including lighting, ventilation and insulating systems should be protected against the corrosive action of acid vapours. Electric switches and motors (fans, refrigerators) should be spark-resistant, and non-sparking tools should be used. Smoking should be prohibited in or near storage areas.

Handling

All persons handling concentrated sulfuric acid should be specially trained in its hazards and safe handling. Wear suitable protective clothing and wash after handling. Handle on an acid-resistant surface designed to contain spills. Safety showers and eye-wash fountains should be available wherever concentrated sulfuric acid is handled.

Dilution of acid should always be carried out by adding acid to water, slowly, and with constant stirring. Water should never be poured on sulfuric acid since this may cause an explosive reaction and splattering of the acid.

Carboys or drums of sulfuric acid should be emptied by gravity or by siphon — never by pressure. Employees opening such containers should wear suitable protective clothing.

Clean-up of Spill or Leak

Persons participating in the cleaning of a spill or leak should be adequately trained. The contaminated area should be immediately zoned off and ventilated thoroughly. For small spills, sulfuric acid should be neutralized carefully with sodium bicarbonate, soda ash (sodium carbonate), slaked lime (calcium hydroxide) or suitable materials, and washed down with large amounts of water. Alternatively, sulfuric acid should be absorbed in vermiculite, dry sand, earth or a similar material, and shovelled into containers for disposal. Several chemical and laboratory supply companies market spill clean-up kits which can conveniently be kept on hand in case of small spills.

Disposal

Federal, provincial or local regulations should be reviewed prior to disposal of waste sulfuric acid or neutralized material. Untreated

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waste sulfuric acid or acid-contaminated water must never be discharged directly into sewers or surface waters. Following neutralization either at the spill site or at a waste management facility, the resultant sludge can be disposed of at a secured landfill. Recovery and reuse of spent sulfuric acid may be an alternative to disposal[21].

VI. FIRST AID

The following general procedures are suggested [7,10,20] for first aid involving overexposure to sulfuric acid:

Inhalation
Remove the victim to fresh air and keep at complete rest. Begin artificial respiration immediately if victim is not breathing. Mouth-to-mouth contact should be avoided since first aiders may be exposed to the chemical within the victim's lung or vomit. Administration of oxygen by a person trained in its use is essential and may prevent fluid accumulation in the lungs. Seek medical attention immediately.

Skin
Give first aid without delay. Seek medical attention immediately. Thoroughly and speedily wash down the victim under a cold shower or hand-held hose, while at the same time protecting his or her eyes from contamination. Continue washing for at least 15 minutes. Remove all contaminated clothing. First aiders should take precautions for their own safety when handling contaminated clothing. Apply nothing (other than water or ice) to burned areas without specific direction from a physician.

Eyes
Wash thoroughly under a gentle stream of water for at least 15 minutes ensuring that the victim's eyelids are held open and that the eyes are moved slowly in every direction. If pain persists, repeat washing process for 15 more minutes or until pain stops. Take care not to rinse contaminated water into the non-affected eye. Seek medical attention immediately.

Ingestion
Remove the victim to a quiet, cool and well-ventilated area and keep at complete rest. Do not induce vomiting but rinse the mouth liberally with cold water. If victim is conscious, have victim drink as much water as possible. The victim may also drink controlled quantities of milk, milk of magnesia or emollients such as vegetable oil or a raw

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egg. Never give anything by mouth to an unconscious person. Transfer victim to hospital immediately.

Note: Consult a physician and/or the nearest Poison Control Centre for all cases of ingestion or eye and skin contact and all but trivial cases of inhalation. All first aid procedures should be periodically reviewed by a physician familiar with the material and its conditions of use in the workplace.

VII. EXPOSURE LIMITS

In many Canadian jurisdictions, exposure limits are similar to the Threshold Limit Values (TLVs) recommended by the American Conference of Governmental Industrial Hygienists (ACGIH). For sulfuric acid the 1986-87 recommended TLVs are:

1. Threshold Limit Value-Time Weighted Average (TLV-TWA) =
   1 milligram per cubic metre (mg/m^3) or 0.250 parts per million (ppm):

   This is "—the time-weighted average concentration for a normal 8-hour workday and a 40-hour workweek, to which nearly all workers may be repeatedly exposed, day after day, without adverse effect."

Certain Canadian jurisdictions have adopted the entire set of ACGIH TLVs for chemical substances by reference in their regulations. Others use the TLVs as guidelines for control of airborne contaminants. Still others specify exposure limits for chemical substances, including sulfuric acid, in their regulations. Since the manner in which exposure limits are established, interpreted and implemented can vary among the jurisdictions, detailed information should be sought from the appropriate government agency in each jurisdiction.

According to the preface in the ACGIH booklet:

"Threshold limit values refer to airborne concentrations of substances and represent conditions under which it is believed that nearly all workers may be repeatedly exposed day after day without adverse effect. Because of wide variation in individual susceptibility, however, a small percentage of workers may experience discomfort from some substances

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at concentrations at or below the threshold limit; a smaller percentage may be affected more seriously by aggravation of a pre-existing condition or by development of an occupational illness."

"Threshold limits are based on the best available information from industrial experience, from experimental human and animal studies and, when possible, from a combination of the three."

"The TLV-TWA should be used as guides in the control of health hazards and should not be used as fine lines between safe and dangerous concentrations." (Reproduced by permission of the ACGIH).

Warning Properties of Sulfuric Acid at the Exposure Limit
For certain substances, odour or irritant properties may be useful as a short-term indicator of possibly hazardous conditions. Sulfuric acid has an odour threshold of greater than 1 mg/m^3[1]. Sulfuric acid is considered to have poor irritant warning properties[1].

Exposure Limits in Other Nations
The approaches or mechanisms for establishing and applying occupational exposure limits can vary widely from country to country. Information on exposure limits in a number of foreign jurisdictions is available from CCOHS.

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VIII. CHEMICAL AND PHYSICAL PROPERTIES

CAS registry number	7664-93-9
Chemical formula	H_2O_4S
Chemical structure	H_2SO_4

Physical Properties

Boiling point	290°C (554°F) for 100% acid
Density	1.84 (water = 1) for 100% acid
Solubility	miscible (soluble in all proportions) in water
Vapour pressure	less than 0.001 mm Hg at 20°C
Vapour density	3.4 at 290°C (air = 1)
Odour threshold	greater than 1 mg/m^3

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Note: Additional references on this subject are available from CCOHS upon request.

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